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Research Article

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Preparation Cobalt Ferrite–Silver Nanocomposite Via Green Chemistry Approach

Yeşil Kimya Yaklaşımıyla Kobalt Ferrit-Gümüş Nanokompozit Hazırlama

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ABSTRACT

Nanocomposites are formed by joining two or more materials, at least one of which must have a size in the nanometer range (1 nm -100 nm). In this study, cobalt ferrite-silver nanocomposite was prepared with a green synthesis approach. The aim was to combine the magnetic properties of cobalt-ferrite nanoparticles with both the antimicrobial and conductivity properties of silver nanoparticles. Thus, the prepared material can be used for biological, optical, electrical, and magnetic applications. Cobalt ferrite nanoparticles were prepared using the co-precipitation method. Silver nanostructures were incorporated into cobalt ferrite nanoparticles using waste grass extract. Scanning Electron Microscope (SEM), Infrared Spectrometer, UV-VIS Spectrometer, X-ray Diffraction (XRD) Spectrometer, Dynamic Light Scattering (DLS) Technique were used for characterization studies.

Key Words

Cobalt ferrite NPs, silver NPs, green chemistry, nanocomposite.

ÖZ

Nanokompozitler, en az birinin nanometre aralığında (1 nm – 100 nm) bir boyuta sahip olması gereken iki veya daha fazla malzemenin birleştirilmesiyle oluşturulur. Bu çalışmada yeşil sentez yaklaşımı ile kobalt ferrit-gümüş nanokompozit hazırlanmıştır. Amaç, kobalt nanoparçacıkların manyetik özelliklerini gümüş nanoparçacıkların hem antimikrobiyal hem de iletkenlik özellikleriyle birleştirmekti. Böylece hazırlanan malzeme biyolojik, optik, elektriksel ve manyetik uygulamalar için kullanılabilir. Kobalt ferrit nanoparçacıkları, birlikte çöktürme yöntemi kullanılarak hazırlandı. Gümüş nanoyapılar, atık çimen özütü kullanılarak kobalt ferrit nanoparçacıklarına dahil edildi. Karakterizasyon çalışmaları için Taramalı Elektron Mikroskobu (SEM), UV-VIS Spektrometresi, X-ray Kırınım (XRD) Spektrometresi, Dinamik Işık Saçılımı (DLS) Tekniği kullanıldı.

Anahtar Kelimeler

Kobalt ferrit NPs, gümüş NPs, yeşil kimya, nanokompozit.

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INTRODUCTION

Nanoscience is an interdisciplinary and exciting field that relies on the nanoscale fabrication of materials. With the development of nanoscience, the concept of nanotechnology was born, and essential steps have been taken in the field of technology and biotechnology in the last decades. Nanotechnology specifically involves the synthesis of nanomaterials of various sizes, morphologies, and geometries. The fact that the nanoscale increases the functionality and properties of materials compared to the macro scale has made nanomaterials interesting in science and technology [1]. Researchers have proven the high efficiency and functionality of nanomaterials through their research in various fields such as health, environment, catalysis, chemical industry, electronics, biomedical, cosmetics, optics, health, mechanics, food and feed, aerospace and defense industries, etc. [2]. Nanoparticle production is the most critical part of nanotechnology because some desired properties occur at the nanoparticle, nanocrystalline, and nanolayer levels [3]. Nanoparticles (NPs) can be classified according to various contents. The most widely used ones are plasmonic, magnetic nanoparticles and quantum dots, etc. Nanoparticles formed by the aggregation of noble metal atoms such as Au, Ag, and Pt become unique tools for biosensing and bioimaging applications thanks to their surface plasmon resonance (SPR) absorption properties. High stability and conductivity properties have made these nanoparticles desirable in the manufacturing and development of electronic devices [4]. Among the plasmonic nanoparticles, especially silver nanoparticles, have cheap, catalytic, light, and antimicrobial properties [5]. Recently, environmental friendly methods have been developed to synthesize metal nanoparticles via plant-mediated [6] or fruit-mediated approach [7] as an alternative to well-established chemical processes [8]. On the other hand, magnetic nanoparticles containing metals such as Co, Fe, Ni have become attractive for their use in biomedical applications (hyperthermia treatment, drug delivery, and magnetic resonance imaging, etc.) thanks to their magnetic properties [9]. Finally, quantum dots (QDs), nanometer-sized particles composed of organic or inorganic materials, have an essential role in immunoassay, biosensing, and bioimaging studies due to their luminescence and fluorescent properties [10].

Nanocomposite materials (NCs) are composites in which at least one of the components has a size in the nanometer range (1 nm = 10^{-9} m). These materials have been produced as favorable alternatives to address the specific shortcomings of microcomposites and monolithics. However, the elemental composition and stoichiometry control of the nanocomponent is the most important challenge in the preparation of the nanocomposite. The use of nanoparticles is very common, especially in the preparation of nanocomposites. Nanoparticles incorporated into the polymer ceramic or metallic matrix enable the new material to be enriched in terms of electrical stability, thermal conductivity, mechanical strength, and optical properties [11].

Due to the environmental and economic disadvantages of conventional physical or chemical methods used in nanoparticle preparation, scientists started a new search, and thus green chemistry approach emerged in nanoparticle synthesis [12]. The chemicals used in these traditional methods often have toxic properties and are expensive. Therefore, in the developed green chemistry approach, biological resources are used for the formation of nanoparticles. The key point of this approach is the use of renewable materials and environmentally friendly compounds as reducing/capping agents to synthesize nanoparticles. Different biomolecules such as vitamins, yeasts, enzymes, algae, biodegradable polymers, and microorganisms are used as reducing/stabilizing agents to synthesize NPs, but also plant parts such as leaves, stems, fruits, bark, roots are used for the same purpose [1].

In this study, cobalt ferrite-silver ($CoFe_2O_4$-Ag) nanocomposite was prepared. Cobalt ferrite nanoparticles were prepared traditional co-precipitation method. Silver nanostructure at nanocomposite was prepared by using a green method; for this purpose, waste material (grass) extract was used as a reducing agent and stabilizer.

MATERIALS and METHODS

Preparation Cobalt Ferrite ($CoFe_2O_4$) NPs

Cobalt Ferrite ($CoFe_2O_4$) NPs were synthesized by the co-precipitation method [13]. 0.81 g $FeCl_3.6H_2O$ (Sigma-Aldrich, USA) and 0.36 g $CoCl_2.6H_2O$ (Sigma-Aldrich, USA) were mixed in 3.12 mL oxygen-free deionized water in a mole ratio of Co(II): Fe(III) 1:2. To this solution, 50 µL of concentrated HCl solution was added for better dissolution of the metal salts. Then, this mixture was added to 31.25 mL of 1.5 M NaOH solution at 80 °C with stirring. After stirring for 1 hour at the same temperature, the black precipitate of bare Cobalt Ferrite ($CoFe_2O_4$) NPs was collected by a magnet and washed three times with deionized water. Cobalt Ferrite ($CoFe_2O_4$) NPs were dispersed in 50.0 mL oxygen-free deionized water.

Table 1. Optimization studies on the volume of $CoFe_2O_4$ NPs, amount of $AgNO_3$, the volume of extract, temperature (T) in both first (1.) and second steps (2.), and magnetic separation after the first step.

Sample	$CoFe_2O_4$ NPs (mL)	1. Amount of $AgNO_3$ (M, mL)	1. Volume of Extract (mL)	1. T (°C)	Magnetic Separation	2. Amount of $AgNO_3$ (M, mL)	2. Volume of Extract (mL)	2. T (°C)
1st	0.2	0.01, 2.5	3.0	50	No	-	-	-
2nd	0.2	0.01, 0.5	3.0	50	Yes	0.01, 2.0	3.0	50
3rd	0.2	0.01, 0.5	3.0	90	Yes	0.01, 2.0	3.0	90
4th	0.2	0.02, 0.5	6.0	90	Yes	0.02, 2.0	6.0	90
5th	0.2	0.02, 0.5	3.0	90	Yes	0.02, 2.0	3.0	90
6th (AgNPs)	-	0.02, 2.5	3.0	90	No	-	-	-

Preparation Waste Grass Extract

Dry grass-based waste obtained from Middle East Technical University campus was also washed twice with deionized water. Afterward, it was kept in a 70% alcohol (EtOH) - water mixture for two minutes and washed twice with sterilized deionized water and dried. In a clean beaker, 15 g of clean, dry grass and 150 mL of sterilized deionized water were boiled for 10 minutes. The resulting extract was filtered by using Whatman® Cellulose Filter Paper No. 42 and Syringe Filter Unit using 0.45 µm. The resulting yellow-green filtrate was stored at 4 °C [5].

$CoFe_2O_4$–Ag Nanocomposite Preparation via Green Chemistry Approach

In the first step, 200 µL of $CoFe_2O_4$ solution and 3.0 mL of waste grass (prepared at the previous part) extract were diluted to 20.0 mL with deionized water, and the temperature was increased to 90 °C by mixing. At this temperature, 0.5 mL of 0.02 M silver nitrate (Sigma-Aldrich, USA) solution was added, and stirring was continued for 15 minutes. The particles were collected with the help of magnets. In the second step, the particles collected by the magnet were dispersed in 17.0 mL of deionized water, and 3.0 mL extract was added to this mixture. The stirring and heating process applied in the first step was repeated. 2.0 mL of 0.02 M silver nitrate solution was added, and stirring was continued for 15 minutes at 90 °C. Then, the obtained nanocomposite was washed three times by the magnetic separation method and dispersed in deionized water. Using various silver nitrate concentrations, extract amounts, and different reaction temperatures, optimization studies were carried out [5].

RESULTS and DISCUSSION

The main purpose of this study was to obtain $CoFe_2O_4$-Ag nanocomposite. For this purpose, optimization studies were carried out. Firstly, the physical properties of the obtained nanocomposites were investigated. The optimization study conditions applied are given in Table 1. For the

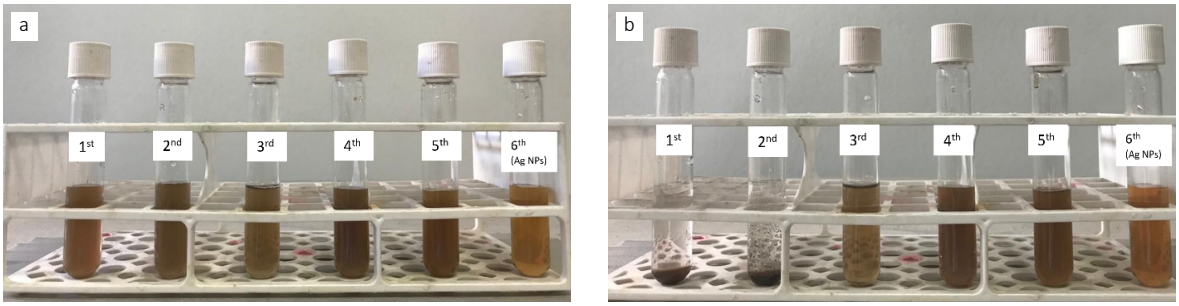

Figure 1. a) Photograph of $CoFe_2O_4$-Ag NCs. (1st, 2nd, 3rd, 4th, and 5th) samples, and 6th (AgNPs) after preparation, b) Photograph of $CoFe_2O_4$-Ag NCs. (1st, 2nd, 3rd, 4th, and 5th) samples, and 6th (AgNPs) after 24 hours.

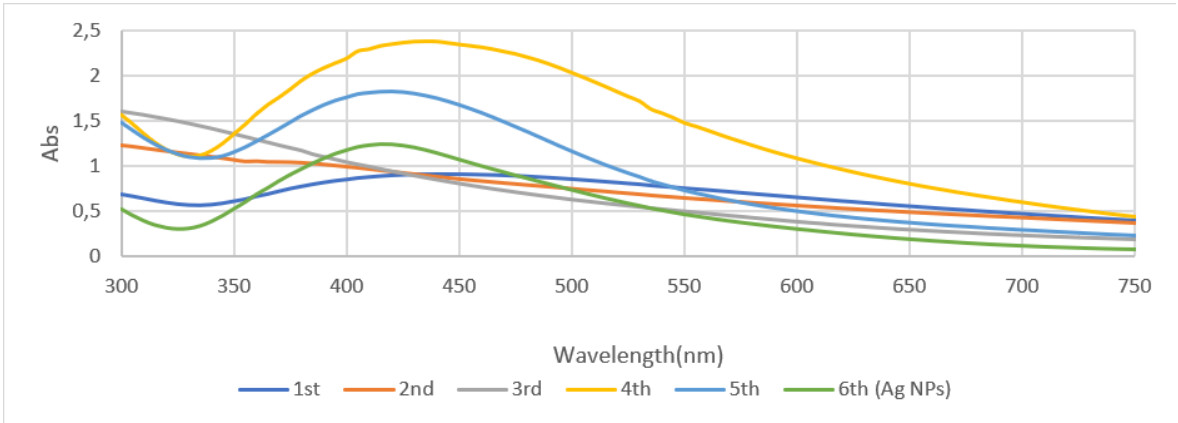

Figure 2. UV-VIS absorption spectra of $CoFe_2O_4$-Ag NCs. (1^{st}, 2^{nd}, 3^{rd}, 4^{th}, and 5^{th}) and 6th (Ag NPs) prepared under different optimization conditions.

1^{st} sample, a single-stage was applied at 50 °C to consume less material. For the 2^{nd} sample, both steps were applied at the same temperature, and the amounts given in Table 1 were used.

For the 3^{rd} sample, the temperature was increased to 90 °C; for the 4^{th} and 5^{th} samples, while the molarity of the silver nitrate solution was increased at the same temperature, different extract amounts were used. In order to compare the samples according to their appearance, only silver nanoparticles were synthesized with the green chemistry approach. Finally, for the 6^{th} sample, Ag NPs were synthesized by the same method (without $CoFe_2O_4$ NPs) to compare the presence of Ag NPs in the nanocomposite samples.

Photographs of five samples and Ag NPs solution are shown in Figure 1a. These solutions were kept for 24 hours at room temperature. The final state of the samples was photographed after incubation and shown in Figure 1b. Compared with Figure 1b, the stability of samples 3, 4, and 5 is higher than the others and is closer in appearance to Ag NPs solution.

The UV-VIS absorbance spectra of the nanocomposites and Ag NPs synthesized using the green chemistry approach are shown in Figure 2. Quartz cuvette and T80+ UV-VIS Instrument (PG Instruments Ltd.) were used for UV-VIS spectrometry measurements. When the spectra are examined, the results support the photographs given in Figure 1b. While the 3^{rd}, $4^{th,}$ and 5^{th} samples give maximum absorbance between 420-490 nm, the absorbances of the 1^{st} and 2^{nd} samples in the same region are quite weak. Especially when the spectrum of 1^{st} sample was compared with the spectrum of Ag NPs, it was observed that no Ag nanostructure was formed. Therefore, the formation of Ag

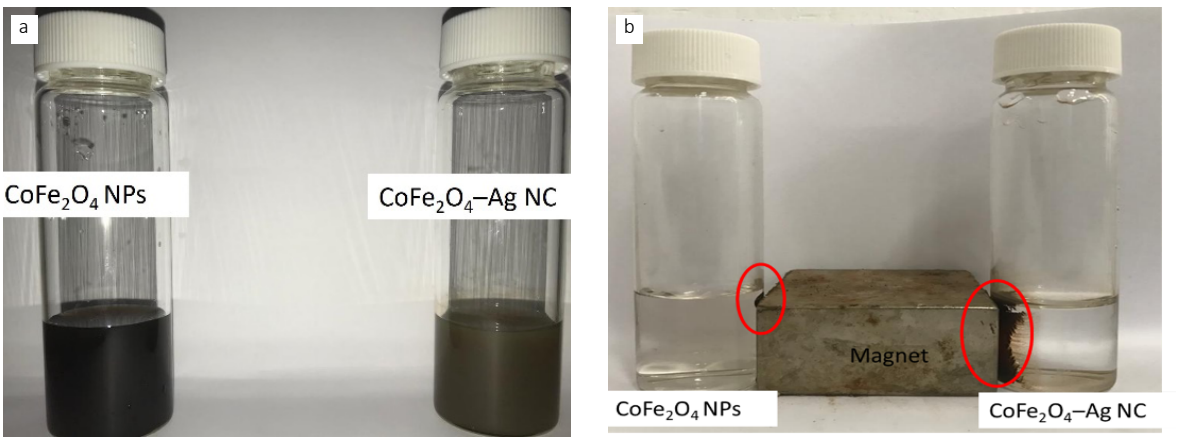

Figure 3. a) Color differences between $CoFe_2O_4$ NPs and $CoFe_2O_4$-Ag NCs. (5^{th} sample) b) Behaviors of $CoFe_2O_4$ NPs and $CoFe_2O_4$-Ag NCs. (5^{th} sample) under the magnetic field after 10 minutes later.

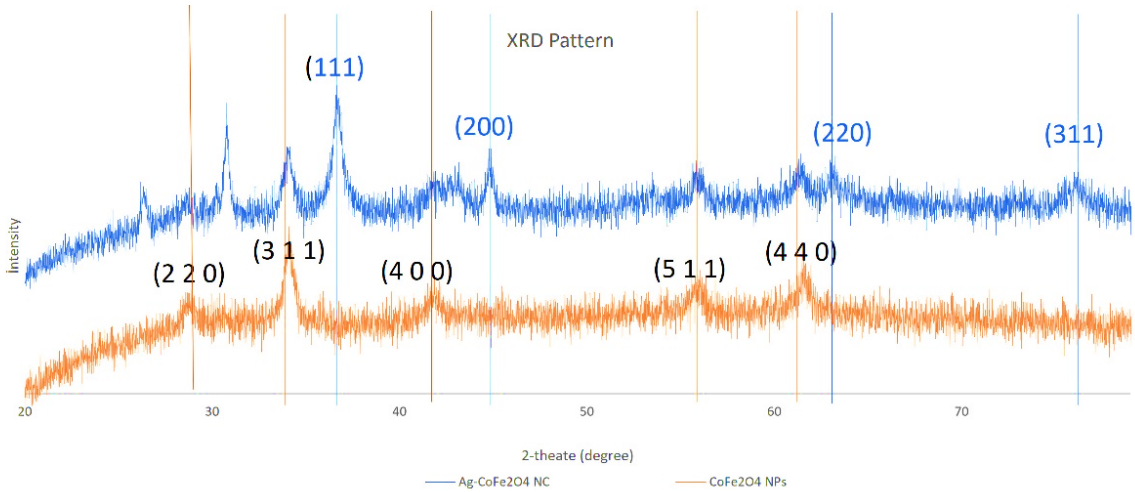

Figure 4. The XRD pattern $CoFe_2O_4$–Ag NC (blue line) and $CoFe_2O_4$ NPs (orange line).

nanostructure was more effective by applying the synthesis process twice in the experimental procedure.

The 5th sample gave the maximum absorbance at 420 nm having the most similar absorbance to the spectrum of the reference 6th (Ag NPs) sample (green line) whereas, the 4th sample has a broader spectrum as an implication of larger size distribution (Figure 2). That is why the characterization studies were applied to the 5th sample.

According to Figure 3a, the color of the solutions changed from dark bright brown to opaque light brown after nanocomposite formation. In other words, this color change showed that silver nanostructures were formed.

The behavior of the prepared nanocomposite under the magnetic field is shown in Figure 3b. 10 minutes after the magnet was placed next to the $CoFe_2O_4$ NPs and $CoFe_2O_4$-Ag NCs solutions, both nanostructures were attracted by the magnet (shown in red circle), and the supernatants remained colorless. In particular, the absence of Ag NPs solution color in the supernatant of the composite solution indicates that silver and magnetic particles form composites, and the nanocomposite shows magnetic properties.

To confirm the crystal structure of nanocomposite and $CoFe_2O_4$ NPs, XRD analysis was carried out by using Rigaku Mini-Flex X-ray powder Diffractometer (XRD) source of Cu-Kα line (λ=1,54056 Å). According to the JCPDS card no 22-1086, cobalt ferrite pattern exhibits five peaks located between 2-theta = 20 and 2-theta = 80 as follows: 30.79, 34.90, 42.14, 56.02, 62.00 are related , (2 2 0), (3 1 1), (4 0 0), (5 1 1), (4 4 0) (hkl) planes, respectively (orange line). The XRD pattern of $CoFe_2O_4$–Ag NC is shown in Figure 4 (blue line). The diffraction lines located 36.74, 44.90, 63.20, and 76.59 are related to the (111), (200), (220), and (311) (hkl) planes of metallic silver crystal, respectively. Additionally, peaks of cobalt-ferrite are located in the XRD pattern of $CoFe_2O_4$–Ag NC. (JCPDS cards no 4-0783 and 22-1086 prove this structure) [14,15].

The SEM images and EDX patterns of $CoFe_2O_4$ NPs and $CoFe_2O_4$–Ag NCs are given in Figures 5a and 5b, respectively. QUANTA 400F Field Emission Scanning Electron Microscopy (METU Central Laboratory) was used for the characterization of $CoFe_2O_4$ NPs and $CoFe_2O_4$–Ag NCs. Cobalt ferrite nanoparticles are seen as agglomerate in Figure 5a due to their magnetic properties. $CoFe_2O_4$ NPs are decorated with Ag NPs after nanocomposite formation, as seen in Figure 5b. The white dots on the sample image show metallic silver particles. According to the SEM image (Figure 5b), the Ag NPSs are homogeneously dispersed in the cobalt ferrite agglomerate. Also, the EDX pattern proves the presence of metallic silver.

Dynamic Light Scattering (DLS) was used to measure the agglomeration dimensions of the formed nanocomposites (Malvern Mastersizer 2000). DLS measurements of $CoFe_2O_4$ NPs and $CoFe_2O_4$–Ag NCs are shown in Figure 6a and Figure 6b, respectively. According to the results of the measurements, the number average size of $CoFe_2O_4$ NPs was 411.4±50.8 (d.nm). On the other hand, the number avera-

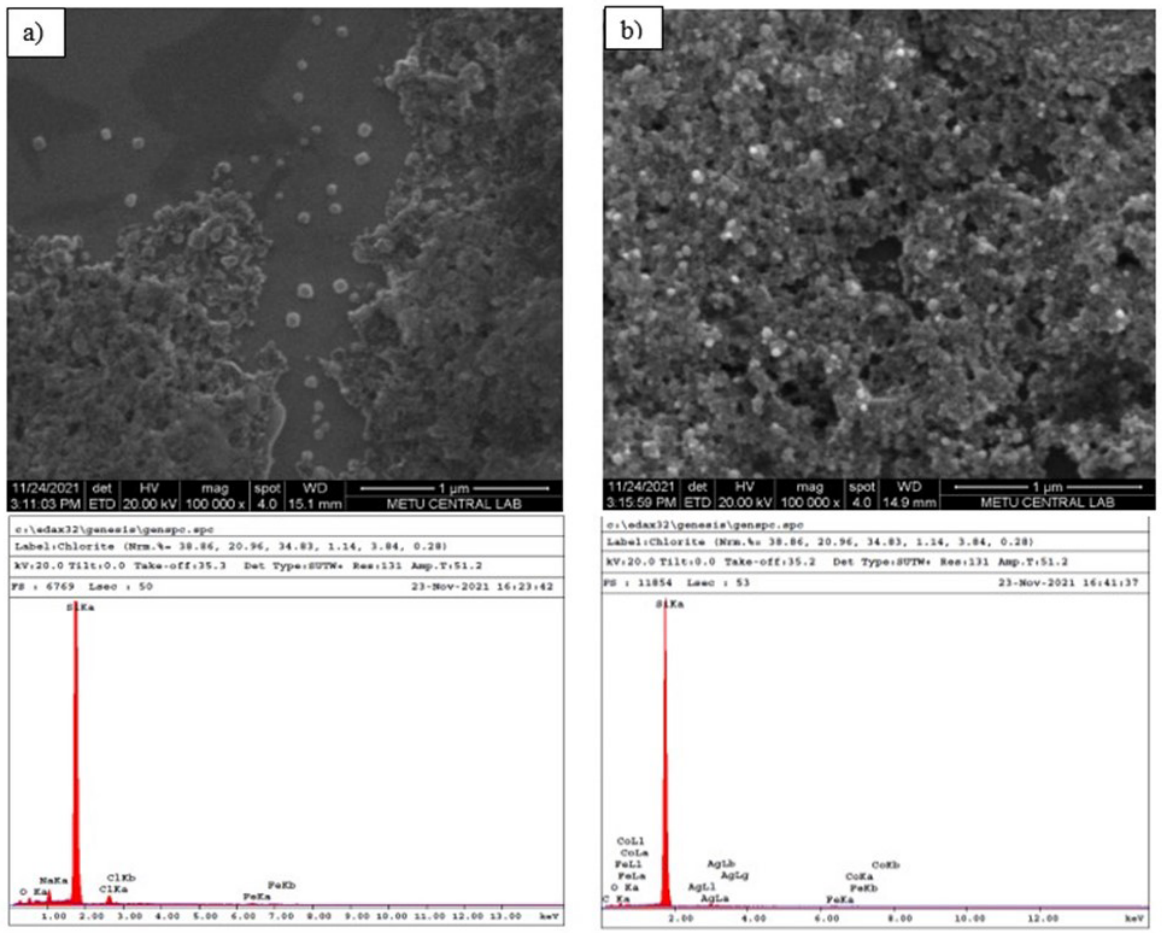

Figure 5. a) SEM images and EDX pattern of $CoFe_2O_4$ NPs b) SEM images and EDX pattern of $CoFe_2O_4$–Ag NCs.

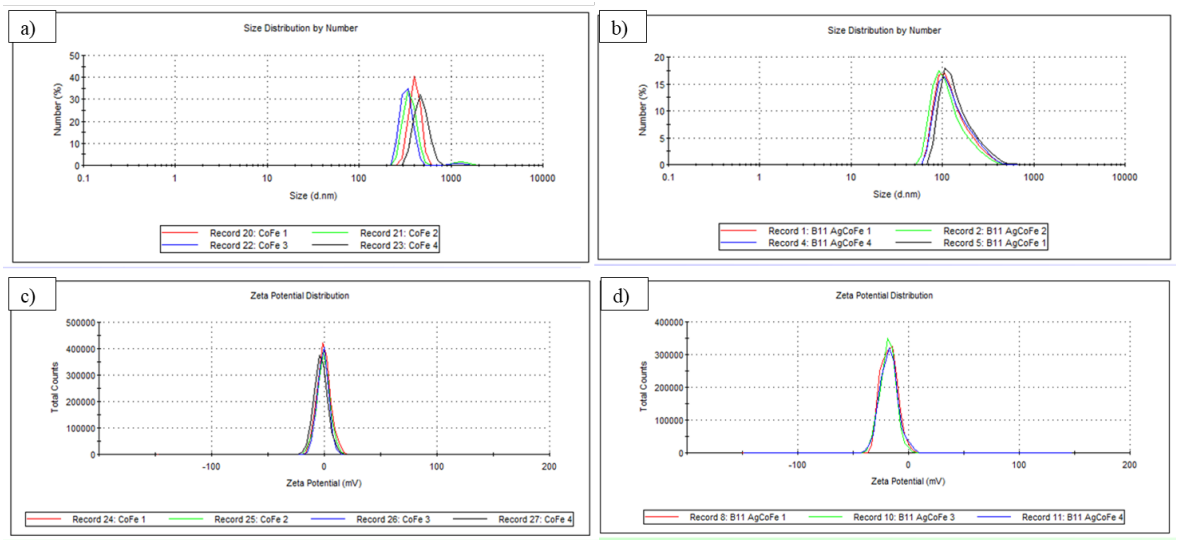

Figure 6. DLS measurement of the number average size of a) $CoFe_2O_4$ NPs and b) $CoFe_2O_4$–Ag NCs. Zeta measurements of c) $CoFe_2O_4$ NPs and d) $CoFe_2O_4$–Ag NCs.

ge size of $CoFe_2O_4$–Ag NCs was measured as 134.4±8.9 (d.nm). Therefore, the agglomeration decreased after nanocomposite formation.

The zeta potentials of $CoFe_2O_4$ NPs (Figure 6c) and $CoFe_2O_4$–Ag NCs (Figure 6d) were measured as -1.42±1.19 mV and -18.0±0.5 mV, respectively. After the formation of the nanocomposite, the surface charge became more negative. This change shows the change in the surface of the nanocomposite structure. At the same time, the low agglomeration level of the nanocomposite in the DLS measurement results supports the increase in the repulsion force due to the electrostatic effect and the decrease in the agglomeration of the magnetic particles.

CONCLUSION

Nanocomposite material was prepared in this study. The prepared material has magnetic, antimicrobial, and plasmonic properties. This has been proven by characterization studies. It has become more functional for many application areas than its microsize or discrete particle states. Therefore, they can be used in many fields such as biomedical, electronics, environmental, etc. Another point of view in the study was to minimize the use of chemicals. Optimization studies were carried out for this purpose. The use of the green synthesis approach in the formation of metallic silver nanostructures has made the composite structure environmentally friendly. With the use of waste grass, the use of dangerous and expensive chemicals has decreased. The constant availability of grass has also made this procedure attractive.

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